

LIBERATION OF HYDROGEN AND OXYGEN TOGETHER ON THE ELECTRODES DURING ELECTROLYSIS ACCOMPANIED BY ELECTRODE GLOW

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ABSTRACT. The gas liberated at the cathode after cathode glow sets in during electrolysis has been found to contain a large proportion even as high as fifty per cent by volume of oxygen. The total gas liberated is also found to be substantially more than that stipulated by Faraday's law. Actual data using various salts in a simple *U*-tube apparatus have been presented. The above type of abnormal behaviour is shown even in 'incipient glow', i.e. when there is no visible glow but other characteristics which generally accompany glow. Imposition of a magnetic field is found to reversibly diminish the glow as also the current to a considerable extent. A tentative mechanism based on microelectric discharges in small pockets of high resistance caused by vapour nuclei formation is suggested; these microdischarges probably generate ion radicals and also electrons from water and the latter may break down more water molecules into ion radicals by collision.

It is well known that brisk electrolysis starts from the decomposition potential of about 2 volts onwards. On increasing the voltage further it is generally thought that the only thing which happens is that more current passes with consequent more liberation of Ohmic heat and increased electrolysis. This is however not entirely correct. On increasing the voltage a point is reached in the region of a couple of hundred volts where the following happens. The current goes on increasing with time, and then after a definite time depending on the initial temperature the current value drops down steeply, as is shown for a typical case of potassium chloride solution in figure 1. A convenient set-up for such experiments is shown in figure 2. This sudden drop in current value is accompanied by a change of pattern of the gas evolution at the cathode. The gas so long being liberated as the usual stream of fine bubbles now changes into big bubbles in more or less volleys. At the same time the turbulence going on in the intermediate region calms down. At this stage the cathode (for some electrolytes, the anode) usually starts glowing and sometimes makes a hissing sound; if the glow does not start at this stage, it can be usually made to start if the cathode is removed from the solution and is immediately put back into the same place. Usually, the cathode glows, but if the anode is smaller than the cathode (i.e. has higher current density), the

glow may appear on the anode instead of the cathode; by suitable adjustment of condition even both the electrodes may be made to glow simultaneously. The above has already been briefly reported by the author in a preliminary note. However, the author collected the gas liberated on the electrodes and measured and analysed it. The results are highly unexpected and surprising, and the present note makes a preliminary report of the same.

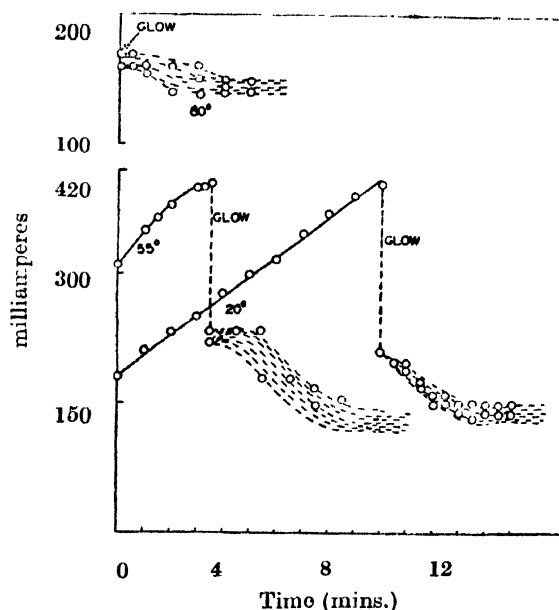


Figure 1. Production of Glow at the platinum cathode on electrolysis of 0.2 N KCl solution.

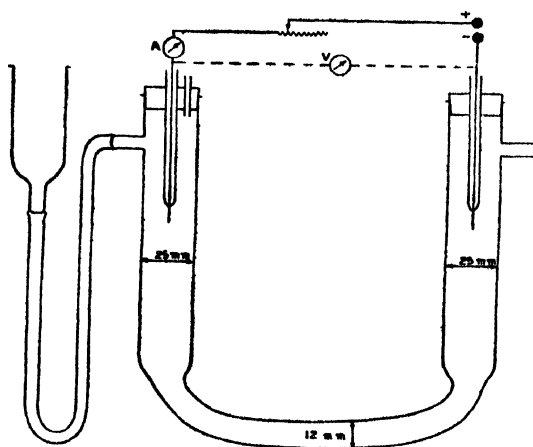


Figure 2.

COMPOSITION OF THE GAS

The gas liberated on the cathode on analysis was found to contain both hydrogen and oxygen. However, the oxygen content varied widely from electrolyte to electrolyte and to some extent in different runs with the same electrolyte. Sometimes the gas collected over the cathode could be exploded leaving only a small residue, and at other times the gas could not be exploded by an electric spark. However, the collected gas on analysis in a Hempel apparatus always showed a considerable quantity of oxygen; some typical results are presented in table-1. It is surprising to find a considerable quantity (16 to 50%) of oxygen in the gas liberated at the cathode side. The gas liberated on the non-glowing anode side was also similarly analysed. The gas liberated on the anode during the induction period (i.e. before the cathode starts glowing and big bubbles start forming) was found to be composed of oxygen only. However, as soon as the glow phenomenon sets in, the gas at the anode contained a considerable quantity of hydrogen along with oxygen, though the total volume was considerably less than that liberated on the glowing cathode side. The total gas (cathode+anode) contained a 2:1 ratio of hydrogen and oxygen except for barium chloride (vide last six data of Table 1). The lower oxygen liberation for barium chloride is probably due to some side reactions and/or chlorine liberation.

FARADAY'S LAW

A most surprising feature of the data shown in table 1 is that in many cases the volume of gas collected even only on the cathode side was found to be in considerable excess of the total volume of electrolytic gas expected from Faraday's law (V_F) not to speak of the total gas (cathode+anode) liberated. Evidently, Faraday's law has nothing to do with this reported phenomenon and a mechanism different from the normal ionic conduction mechanism must be operating. Since the quantity of gas liberated overrides the barrier imposed by Faraday's law, the phenomenon in question may have possibility for cheaper industrial production of hydrogen. The maximum yield so far observed under our experimental conditions is in excess of Faraday's law by a factor of about two. However, it is likely that this factor, may go way up under changed conditions of higher voltage, current intensity and so on. The new phenomenon may be called glow electrodecomposition or simply electrodecomposition or glowlysis to distinguish it from ordinary electrolysis on the one hand and from glow electrolysis (the electrode is in the gas phase at a much higher minimum operating voltage) on the other.

EFFECT OF MAGNETIC FIELD

The cathode was placed between the poles of an electromagnet (maximum field strength about 15,000 gauss) and the effect of the magnetic field was studied.

The magnetic field was found to have a strong influence on the glow in two respects. The intensity of glow decreased with increase of magnetic field strength, the incandescent platinum wire becoming paler and paler with increase of the magnetic field intensity. At sufficiently high applied magnetic field strength the glow tended to disappear altogether. In fact, it was found difficult to start a glow if the cathode was in the magnetic field to start with. Secondly, it was observed that the current strength decreased considerably on switching on the electromagnet. The current decreased by about 50 to 100 milliamperes under our conditions of experiment. Evidently, the current carriers are not simple ions but are at least partly ion radicals. Attempt to initiate polymerization by these ion radicals by adding acrylonitrile monomer however failed probably due to the inhibiting action of oxygen.

Table 1

| Electrolyte (0.2 N) | Glow current (average) (Amp.) | Duration (min.) | Theoretical Volume V_F (H + O) (c.c. N.T.P.) | Gas collected (reduced to dry N.T.P.) | | |
|---|--|--------------------|---|---------------------------------------|-----------------------------|--------------------|
| | | | | at Cathode (c.c.) | Oxygen content (c.c.) | Per cent oxygen |
| (NH ₄) ₂ SO ₄ | 0.18 | 20 | 36.0 | 29.4 | 7.5 | 25.5 |
| BaCl ₂ | 0.18 | 20 | 36.0 | 58.2 | 9.7 | 16.7 |
| BaCl ₂ | 0.18 | 20 | 36.0 | 55.9 | 9.4 | 16.8 |
| HCl | 0.13 | 20 | 27.2 | 33.3 | 11.3 | 34 |
| HCl | 0.092 | 20 | 21.2 | 17.3 | 6.9 | 40 |
| NaOH | 0.12 | 20 | 25.1 | 51.6 | 21.8 | 42.3 |
| KNO ₃ | 0.15 | 20 | 31.3 | 45.4 | 23.4 | 51.5 |
| KCl | 0.15 | 20 | 31.3 | 42.9 | 20.3 | 47.1 |
| KCl | 0.15 | 10 | 15.7 | 25.5 | 11.6 | 45.6 |
| KCl* | 0.09 | 5 | 4.7 | 4.2 | 0.4 | 9.5 |
| KCl* | 0.11 | 20 | 23 | 20.2 | 3.5 | 17.3 |
| K ₂ SO ₄ | 0.17 | 20 | 35.5 | 52.4 | 15.5 | 29.6 |
| at Cathode + Anode | | | | | | |
| K ₂ SO ₄ | 0.16 | 21 | 35.1 | 69.3 | 23.3 | 33.7 |
| BaCl ₂ | 0.16 | 10 | 16.7 | 24.6 | 6.2 | 25.1 |
| BaCl ₂ | 0.10 | 15 | 15.7 | 31.3 | 7.4 | 23.5 |
| BaCl ₂ | 0.16 | 19 | 31.8 | 40.7 | 7.3 | 17.8 |
| NaF | 0.21 | 19 | 41.7 | 50.8 | 16.8 | 33.2 |
| NaF | 0.25 | 15 | 39.2 | 49.6 | 16.7 | 33.7 |

*Incipient glow i.e. no visible glow but after the steep drop in current and when the gas is liberated in big bubbles.

MECHANISM

It is difficult to account for the observations on the basis of the normal ionic conduction mechanism. A decomposition of water or water vapour on the glowing platinum to give such a high yield is ruled out on thermodynamic grounds. Besides, this can not account for more than one-third by volume of oxygen at the cathode side. Similarly, the idea of some kind of local action is untenable. However, the sudden drop of current value along with disappearance of turbulence in the intermediate zone at the onset or near-onset of glow is rather significant in the context of the fact that such behaviour is often observed in glow and discharge phenomenon in gases. It is likely that the basic mechanism is very similar to that operating in electric discharge and glow in gases. Further support to this idea is lent by the fact that electrolytic gas in excess of that prescribed by Faraday's law is obtained; this points to some kind of cascading or chain reaction as in electric discharge in gases. The magnetic behaviour indicates the existence of ion radicals.

The following mechanism can be visualized. With temperature approaching the boiling point, vapour nuclei start forming. These may be regarded as microzones of high resistance. The resistance of these microzones being high, high voltage occurs across them. This causes microelectric discharge across these microzones. These microdischarges cause breakdown of water liberating electron ($\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e$). The H_2O^+ probably in its hydrated form decomposes on its way to the cathode ($\text{H}_2\text{O}^+ \rightarrow \text{H}^+ + \text{OH}$) producing oxygen in the cathode gas. The electrons may ionize more water molecules as shown above by collision and a cascading action takes place. Some of these electrons may react with water either by itself or after hydration liberating hydrogen ($e + \text{H}_2\text{O} \rightarrow \text{OH}^- + \frac{1}{2}\text{H}_2$). Thus gases in excess of that prescribed by Faraday's law are liberated. It is however too early to postulate a detailed mechanism.

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REFERENCE

Palit, S. R., 1967, *Indian J. Phys.*, **41**, 860.